

PHOTO-TREATMENT OF PALM OIL MILLS EFFLUENT (POME) OVER Cu/TiO₂ PHOTOCATALYST

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ABSTRACT

The current work reports the use of titania based photocatalysts for the photo-treatment of palm oil mill effluent collected from Felda Lepar Hilir 3, a local source. Different metal loadings of copper viz. 2wt%, 5wt%, 10wt%, 15wt%, 20wt% and 25wt% were doped onto titania employing wet impregnation method. The synthesized catalysts were subjected to physicochemical characterization. Gas pycnometer density measurements revealed that the actual density of catalysts were lower than theoretical density due to the porous structure as proven by the subsequent liquid N₂ physisorption. In addition, X-ray diffraction pattern showed formation of CuO with crystallite size ranging from 41.8 to 49.1 nm upon calcination. Significantly, liquid N₂ physisorption showed that the BET specific surface area of catalysts prepared decreased with wt% of Cu probably due to pore blockage. Moreover, 5wt% Cu/TiO₂ exhibits the largest pore volume, which is 0.049 cm³/g for both adsorption and desorption volume. In the term of pore size, 20wt% of Cu/TiO₂ has the largest adsorption pore size, which is 23.39 nm while 5wt% of Cu/TiO₂ has the largest desorption pore size, which is 19.83 nm. Based on the UV-irradiated photoreaction results, 20wt% Cu/TiO₂ yielded the highest organic degradability (conversion) among all the synthesized catalysts. Overall, 27.0% conversion was achieved within 1 h of photoreaction. Based on the integral method, it seems that the POME photo-reaction followed the 2nd-order reaction. Moreover, 20 wt% Cu/TiO₂ exhibited the highest specific reaction constant at $2.60 \times 10^{-5} \text{ (ppm.min)}^{-1}$. Besides, an optimum catalyst loading were also discovered in current project. For 20wt% Cu/TiO₂, the optimum catalyst loading is 0.83g/L of POME solution. Finally, a longevity test was conducted and it was found that more than 40% of the organic contaminant was decomposed after 7 h of UV-irradiation. Moreover, CO and CO₂ were detected in the gas products from GC analysis. As conclusion, phototreatment for POME shows positive results in current project and is suitable to replace the existing traditional POME method for better efficiency.

Key words: Copper ; Palm oil mill effluent ; Photocatalysis, Titania-;

ABSTRAK

Projek ini melaporkan tentang penggunaan pemangkin titania untuk teknologi proses penguraian sisa buangan kilang sawit (POME) daripada Felda Lepar Hilir 3. Berbeza peratusan of logam copper seperti 2wt%, 5wt%, 10wt%, 15wt%, 20wt% dan 25wt% telah dicampur ke atas titania melalui wet impregnation method. Pemangkin-pemangkin yang disediakan telah dianalisis melalui pelbagai teknik. Gas pycnometer menyatakan kepadatan pemangkin-pemangkin yang disediakan ini lebih rendah daripada pengiraan disebabkan struktur yang berliang dan ini telah disahkan oleh liquid N₂ physisorption. Selain itu, X-ray diffraction menunjukkan CuO formasi dengan ukuran dari 41.8 sehingga 49.1 nm. Seterusnya, liquid N₂ physisorption menunjukkan kawasan permukaan pemangkin yang disediakan semakin mengurang dengan Cu wt% disebabkan penyumbatan liang. Selain itu, 5wt% Cu/TiO₂ mempunyai isi padu liang yang paling besar iaitu 0.049 cm³/g untuk kedua-dua adsorption dan desorption. Untuk saiz liang, 20wt% Cu/TiO₂ mempunyai adsorption liang saiz yang paling besar iaitu 23.39 nm manakala 5wt% Cu/TiO₂ mempunyai desorption liang saiz yang paling besar iaitu 19.83 nm. Berdasarkan keputusan daripada experiment, 20wt% Cu/TiO₂ paling efektif dalam rawatan POME dan telah mengurangkan organik dalam POME sebanyak 27% dalam 1 jam. Berdasarkan integral method, organik-organik dirawat mengikut reaksi 2nd order. Selain itu, 20wt% Cu/TiO₂ juga menunjukkan kadar reaksi yang paling tinggi, iaitu 2.60×10^{-5} (ppm min)⁻¹. Kandungan pemangkin yang paling optima dalam POME juga dicari dalam projek ini, iaitu 0.83g/L. Longevity test telah dijalankan dan 40% organik didapati telah dirawat dalam 7 jam. CO dan CO₂ telah didapati sebagai produk gas daripada experiment ini dengan GC analysis. Akhirnya, teknologi proses penguraian ini menunjukkan keputusan positif dalam project ini dan sesuai untuk menggantikan cara rawatan yang lama untuk keberkesanan yang lebih baik.

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LIST OF NOMECLATURES

a	BET effective cross-sectional area
A	apparent absorbance
c	characteristic constant of the adsorbate
C	BET dimensionless constant
C	Concentration
d	Inter plane distance of crystal
D	Crystalline size (Å)
e-	Negative-electron
h+	Positive-hole
k	Rate constant (min ⁻¹)
kSch	Scherrer constant
m	BET mass of solid catalyst
n	Order (interger)
N	Avogrado constant (6.022×10 ²³ mol ⁻¹)
P	BET partial vapor pressure
P _a	BET ambient pressure
P _o	BET saturated pressure
ppm	part per million (mg/L)
r	BET correlation coefficient
R	BET gas constant (8.314 E7 ergs/K.mol)
-r _A	Photoreaction rate (mg/L.min)
r _k	BET Kelvin radius of pore
r _p	BET actual pore radius
S	BET specific surface area
T	BET ambient temperature
t	time
V _a	BET volume of gas adsorbed at STP
V _{ads}	BET volume of N ₂ adsorbed
V _{liq}	BET volume of liquid
V _m	BET volume of gas absorbed at STP to monolayer coverage
w	Weight fraction
wt%	Weight percent
X	Conversion
β _d	Angular width of half-maximum intensity (degree/°)
γ	BET surface tension of N ₂ (8.85 ergs.cm ² at 77.4 K)
θ	Angle (degree/°)
λ	Wavelength (nm)
ρ	Density

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BJH	Barrett, Joyner and Halenda
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
DH	Dollimore and Heal
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
HRT	Hydraulic retention time
LDH	Layered double hydroxide
MB	Methylene blue
POME	Palm oil mills effluent
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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CHAPTER 1

INTRODUCTION

1.1 Background

Malaysia has been recognised as one of the largest cooking oil producers in the world (Wu et al., 2010) attributed to its tropical climate and abundance of arable land fit for cash crop cultivation. Nonetheless, the growing success of this industry is often overshadowed by massive industrial discharge from its mill. In the year 2008 alone, at least 44 million tonnes of POME was generated in Malaysia (Wu et al., 2010). In a survey carried out by Sime Darby Plantation (2011), on average, one tonne of fresh fruit bunch processed produces about 0.65 tonne of POME. Palm oil mill effluent (POME) contains high concentration of organic matter. The chemical oxygen demand (COD) of POME is typically in the range of 45,000 to 65,000 mg/l whilst 5-days biochemical oxygen demand (BOD) is averaging 18,000 to 48,000 mg/l (Chin et al., 1996). In addition, oil and grease comprised of more than 2,000 mg/l (Chin et al, 1996). Significantly, the COD : N : P ratio is around 750 : 7.3 : 1 (Chin et al, 1996). A more detailed information of POME will be presented in Section 2.2.

To avoid the water bodies being polluted, POME should undergo treatment before discharged into the rivers. Various treatment and disposal methods have been proposed, investigated and commercialized in the past decades to eliminate or reduce POME pollution. The treatment processes include floatation, membrane technology, various aerobic and anaerobic biodegradation and others (Ahmad et al., 2003). However, an ideal treatment process should be cost-effective and most importantly, the process should not leave any hazardous residues or at least reduces the harmful materials to a safe level.

Significantly, for the past two decades, photocatalysis process has been touted as a promising technology and hence widely investigated for application in treating aqueous organic contents (Puzyn & Mostrag-Szlichtyng, 2012). Photocatalysis applies concept of the acceleration of a photoreaction in the presence of a catalyst as well as the UV or visible light irradiation. It is one of the cleanest technologies for the degradation of waste water and any pollutants or contaminant in POME, since most of the contaminants is organic substrate (Fujishima et al., 2000).

The catalyst that is normally used in photocatalysis process is the titanium dioxide(TiO_2)-based material as it possesses low toxicity, low resistance towards corrosion and also a readily-available semiconductor (Amadelli, 2005). According to Fujishima et al. (2000), TiO_2 is an excellent photocatalyst material for environmental purification. The discussion about catalyst, TiO_2 is incorporated in Section 2.4.

The mechanisms of photocatalysis involve the absorption of light-energy (from UV or visible) by photocatalyst. This in turn will trigger the excitation of electrons across the energy gap into the conduction band. In the presence of water, the electron will change into hydroxyl radical which can decompose organic compounds present in the POME. This forms the basic concept that is to be applied in industrial to treat the pollutant in POME (Linsebigler, 1995). The mechanisms of the catalyst is duly highlighted in Section 2.5.

In POME photo-treatment, catalyst plays an important role in assuring the efficiency. A perfect ratio of active metal doped will enhance the performance of the catalyst. Chapter 3 will discuss the method in preparing the catalyst needed for this research, including pre-treating of raw materials, procedure of preparing and the methods to preserve the catalyst. Besides, Chapter 3 will also discuss on the steps to measure the effectiveness of the catalysts.

The results obtained and related discussion are presented in Chapter 4. The POME concentration was analyzed before and after the photo-treatment process employing the techniques described in Chapter 3.

Finally, summary based on the results as well as the recommendation for future works are presented in the Chapter 5.

1.2 Problem Statement

As aforementioned, Malaysia is one of the biggest palm oil producing country in the world. Hence, large scale generation of waste in the form of POME is unavoidable during the extraction of crude palm oil. The effluent contains high biochemical oxygen demand (BOD) liquid waste and chemical oxygen demand (COD) as rightly pointed out by Ahmad et al. (2003). Direct discharge of untreated POME to rivers will cause serious implications to the existing environment. Therefore, it needs to be treated before being released to the waterway.

Among all the treating methods, photocatalysis is chosen in current study due to its efficiency and green pathway. For photocatalysis, the physicochemical properties of catalyst influence the photocatalytic activity. In particular, the percentage of metal loading in catalyst typically influences the catalyst quality. Titania-based photocatalysts have been prepared with various active metal (copper in this study) loadings. To date, there is paucity of information on photocatalyst treatment towards POME. Therefore, the effectiveness of synthesized catalyst forms the pivotal objective the current work.

1.3 Objective

The objective of this study is to undertake systematic analyses into the effects of various photocatalyst formulations towards physicochemical properties and its POME-photodegradation ability.

1.4 Scopes of Study

To meet the objective of the current work, the following scopes of research have been identified:

1. To prepare TiO₂-based photocatalyst with the following composition of active metal using wet co-impregnation method :
 - i) 2 wt%
 - ii) 5 wt%
 - iii) 10 wt%
 - iv) 15 wt%
 - v) 20 wt%
 - vi) 25 wt%
2. To characterize the physicochemical properties of the photocatalysts via:
 - i) X-ray Fluorescence (XRF)
 - ii) X-ray Diffraction (XRD)
 - iii) Density determination
 - iv) Liquid N₂ Physisorption
 - v) Thermogravimetric Analysis (TGA)
3. To conduct photocatalysis of POME with the catalysts prepared to determine the optimum catalyst
4. To analyse the chemical oxygen demand (COD) of POME before and post photoreaction

1.5 Rational and Significance

POME produced during palm oil production is highly polluting if directly discharge into rivers without treatment. Therefore, a good purification or treatment of POME is essential. With better treatment process, the toxicity of the POME will be less harmful to environment or even diminished. Indirectly, this will help to prevent the environment being compromised, as well as maintaining the ecological balance.

This project aims to help in exploring the application potential of photocatalysis process in POME treatment. This will greatly enhance the effectiveness of photocatalysis, not only in treating POME, but also prospectively for other industrial wastewater. This technology has potential to be commercialized for industrial application due to low cost and significantly low energy consumption.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Palm oil industry is one of the leading agricultural industries in Malaysia with an average crude palm oil production of more than 13 million tonne per year (Nour et al., 2011). However, the massive production of this crude palm oil results in even larger amount of palm oil mill effluent (POME), *circa* 44 million tonnes of POME were generated in the year 2008 alone (Wu et al., 2010). Unfortunately, POME is a highly polluting wastewater with high chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Hence, it causes irreversible distress to the water resources if discharge without treatment (Lam & Lee, 2011).

Significantly, common treatment methods employed in Malaysia are ponding system and aerobic digestion (Tay, 1991; Nour et al., 2013). However, both methods have some disadvantages for POME treatment, *i.e.* long retention time for ponding system and high operating cost for aerobic method. Compounded to these, the land scarcities that came along had invigorate the need for the development of new treating technology such as photocatalysis treatment for POME that was introduced in this thesis.

In this chapter, the previous researches related to this topic is critically reviewed in particular research works that report on the effects of different metal loadings towards photoreaction.

2.2 Palm Oil Mill Effluent (POME)

Oil palm is one of the world's most rapidly expanding equatorial crops. Unfortunately, extracting the palm oil via steam-extraction in any existing palm oil mill generates huge amount of palm oil mill effluent (POME). POME is a brownish colloidal suspension with high organic content and moderate temperature (343 to 353 K) as described by Anon (1995). Generally, this waste is hot and acidic in nature and comprised of oil, plant debris, and nutrients. Large palm oil mills typically produce an average of 0.65 tonnes of raw POME for every tonne of fresh fruit bunches processed (Lim et al., 2012). The general properties of POME are listed in Table 2.1. It shows that the COD value of POME is as high as 15 000 to 100 000 mg/L. High COD values indicate high organic contents within the POME.

Table 2.1 The general properties of POME (Kamal et al., 2012).

Physical & Chemical Properties	Unit	Value
Moisture Content	%	93.4
Ash	%	1.06
Total Solid	g	65 – 80
Soluble Fibre	%	SS 1.12
Non Soluble Fibre	%	TS 3.9
COD	mg/L	15 000-100 000

Table 2.2 lists the contents of POME. It shows that POME consists primarily of solid and volatile organic solids at an average concentration of 40 000 mg/L while oil and grease constitute 4000 mg/L. In addition, there are also some metal contents in POME, viz. potassium (2270 mg/L), magnesium (615 mg/L), calcium (439 mg/L) and others. Nonetheless, these inorganic metal contents are considerably lower than the aforementioned organic content.

Due to the hazardous contaminants (cf. Tables 2.1 and 2.2), when POME is discharged into waterways, it can pollute water source that serves as vital drinking water for human and animal populations. More alarmingly, it is also extremely harmful to the aquatic ecology by creating highly acidic environments or causing

eutrophication where excessive algal growth occurs on the surface of the water (Lim et al., 2012).

Table 2.2 The content of POME (Kamal et al., 2012).

Parameter	Average	Metal	Average
pH	4.7	Phosphorous	180
Oil and Grease	4000	Potassium	2270
Total Solids	40500	Magnesium	615
Suspended Solids	18000	Calcium	439
Total Volatile Solids	34000	Baron	7.6
Ammonical Nitrogen	35	Iron	46.5
Total Nitrogen	750	Manganese	2
		Copper	0.89
		Zinc	2.3

*All in mg/l except pH

Moreover, POME also is one of the sources of greenhouse gas (GHG) emissions (Lim et al., 2012). It is well known that POME from the mill site is directly released into open-air holding ponds for remediation and eventually greenhouse gases such as CO₂, CH₄ and H₂S will be released to the air unleashing potentially climate-crippling effects.

To alleviate these catastrophe effects, POME can be utilised for producing value-added chemicals in line with cradle-to-rave concept. According to America Palm Oil Council (2003), POME is an excellent substitute for inorganic fertilizer. Upon treatment, the pH of POME can be raised from 4.0 to *circa* 8.0. Moreover, the BOD is also significantly lower whilst at the same time maintaining the plant nutrients. In terms of fertilizer value, 500 litres of treated POME is equivalent to 1.96 kg of urea (America Palm Oil Council, 2003).

Alternatively, as a potential source of renewable energy, hydrogen (H₂) could be extracted from POME. H₂ is considered as a clean energy as no carbon will be emitted when oxidized (Atif et al., 2005), therefore reducing dependency on the dwindling fossil fuel (Lee, 2012).

2.3 POME Treatments

In Malaysia, most of the palm oil mills use anaerobic digestion for the primary treatment (Tay, 1991). According to Ma et al. (1993), more than 85% the POME producers in Malaysia have adopted the ponding system for POME treatment due to its low capital and operating costs. However, this widely employed method has several disadvantages. One of the disadvantages of ponding system is large land area requirement for treatment process (Nour et al., 2011) as a large pond must be built. Besides, long retention time is also needed for organic contents in the POME to degrade to a safe level (Nour et al., 2011). Usually, the estimated retention time is approximately one to two months. From the environment perspective, emissions of biogas (mixture of CH_4 and CO_2) also poses a major problem to the ozone layer (Nour et al., 2013).

Another common treatment method is aerobic method (cf. Table 2.3). This method is very effective in handling wastewater as it needs shorter retention time (Nour et al., 2013). For instance, Karim and Kamil (1989) found that by using the fungal inoculum, the COD of the POME has recorded more than 95% reduction after 10 to 14 days of fermentation. Besides, Oswal et al. (2002) also found that treating POME with *Yarrowia lipolytica* NCIM 3589 to degrade alkanes contents have provided 95% of reduction in COD within two days. In addition, Vijayaraghavan et al. (2007) disclosed that POME treatment using aerobic oxidation based on an activated sludge process was able to remove COD at higher rate in anaerobically-digested POME as compared to diluted raw POME at hydraulic retention time (HRT) of 60 h. According to Doble and Kumar (2005), one of the primary disadvantages of aerobic method is high energy requirement for aeration, consequently the operating cost will be inflated. Besides, it is also not suitable for land applications due to low inactivation rate of pathogen. Other methods are summarized in Table 2.3, together with their retention time and the corresponding COD reduction percentage.

To overcome these problems, photocatalysis process will be a good choice to replace the aforementioned methods. According to Bahnemann (2004), the advantage of photocatalysis in water purification is the complete decomposition of organics. The effectiveness of POME treatment as the main purpose for the treatment is associated

with organic compound degradation. In terms of energy consumption, ultimately the sun is a continuous and readily available power supply for photocatalysis as the activator needed for this process is visible light or UV radiation (Maria et al., 2011.). Hence, the operating costs will be greatly reduced. Based on these reasons, the photocatalysis process is a potentially valuable technology in POME treatment. Thus, the focus of the current work is to explore the potential of photocatalysis process on POME treatment.

Table 2.3 List of POME treatments.

Treatment process	Retention Time (day)	Reduction in COD (%)	Reference
Anaerobic			
Anaerobic suspended growth processes	35	96	Chin & Wong, 1983
Semi-continuous digester	5.6	75	Cail & Barford, 1985
Anaerobic filter	1	99	Borja & Banks, 1995
Anaerobic fluidized bed reactor	0.25	78	Borja & Banks, 1995
Membrane anaerobic system	3.15	92	Fakhru'l-Razi & Noor, 1999
Semi-commercial closed anaerobic digester	17	>95	Yacob et al., 2006
Completely mixed reactors	50	83	Borja et al., 1995
Tank digester	30	98	Edewor, 1986
Tank digester with certain degree of mixing	30	98	Ugoji, 1997
Modified anaerobic baffled reactor	10	95	Faisal & Unno, 2001
Anaerobic digester	15-16	91	Ma & Ong, 1986
Aerobic			
Pressurized activated sludge process	0.42	98	Ho & Tan, 1988
Aerobic treatment with <i>Yarrowia lipolytica</i>	2	97	Oswal et al., 2002
Activated sludge reactor	2.5	10	Vijayaraghavan et al., 2007
Aerobic treatment with <i>Y. lipolytica</i> þ 0.03 g/L FeCl ₃ þ consortium developed from garden soil	6	99	Oswal et al., 2002
Aerobic treatment with mixed culture	7	>95	Karim & Kamil, 1989
Aerobic treatment with 5% inoculum of <i>Trichoderma viride</i> spores	14	>95	Karim & Kamil, 1989